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MCSCF FOR EXCITED STATES

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ABSTRACT

A method for obtaining equivalent descriptions of many states is described. This method uses a full valence MCSCF to identify the important configurations. These important configurations are then used in limited MCSCF and then followed by single and double excitation CI or POLCI. The treatment of higher states of a given symmetry is also discussed.

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MCSCF FOR EXCITED STATES

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Two basic types of configuration interaction (CI) calculations are routinely used in accurate ab initio calculations. They are the First Order CI¹ (FOCI) and the all single and double excitation CI, CI(SD). In both cases the orbitals are initially optimized using a limited MCSCF. Recent advances in MCSCF Theory² now permit MCSCF calculation containing ~200 CSF's to be performed with little effort in excess of the previous small MCSCF calculations. Thus, it is now possible to optimize the orbitals for a FOCI, by performing a full valence MCSCF (FVMCSCF). If the FOCI is too large and a POLCI³ (a POLCI is best viewed as a FOCI with CSF selection) is to be used or a CI(SD) is to be run, the FVMCSCF can be employed to identify the dominant configurations in the wavefunction. FVMCSCF calculations are performed at various points on the surface, the natural orbitals (NO's) obtained and FVCI repeated in the NO basis. The union of all important configurations is then used in a small MCSCF. This MCSCF is followed by either the POLCI or CI(SD), using the orbitals obtained in the small MCSCF. By performing the FVMCSCF, one simplifies the procedure for identifying the important CSF's which should be included in the MCSCF.

Limited MCSCF calculations followed by CI calculations are a standard treatment for the lowest state in each symmetry. One exception would be when transition moments are desired. In this case a common set of orbitals would be used, but even in this case the separate MCSCF orbital optimization followed by CI is usually performed to calibrate the common orbital set. In principle one could use the same techniques on the higher states of a given symmetry, but in practice new problems arise. As one optimizes an upper root, the description of the lower root is degraded. This can lead to a flipping of these two states and the loss of the upper bound to the desired root.

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Hinze⁴ has proposed optimizing the orbitals based on the averaged field of the states of interest. He also noted that one must compensate for the poorer description of the orbitals by adding additional CSF's. The addition of CSF's to the MCSCF greatly increased the size of the CI(SD) and can quickly make the problem intractable. If the configuration list is not increased, it seems unlikely the states treated by averaged field method will be as accurate as those state for which an independent optimization of the orbitals is performed. Averaging all states of interest would encounter problems if all states but one were well described by one set of orbitals. The average field technique would treat one state more poorly than the rest. While the averaged field technique avoids the problem of variational collapse, it may not treat all states equivalently for a configuration list small enough to allow a CI(SD). Ideally, one would like to perform an independent variational calculation on each state. Grein⁵ has noted if variational collapse begins to occur, a small CI would indicate which CSF's are needed to keep the lower roots in place. While in principle the MCSCF could become prohibitively large, in practice this does not appear to be a problem. We find for ionic systems such as BeO, MgO, and CaO that FVMCSCF - FOCI calculations yield poor separations between the low-lying states and instead a limited MCSCF followed by CI(SD) was employed. The addition of the CSF's needed to prevent variational collapse can make the CI(SD) prohibitively large. Also for a FVMCSCF - FOCI if an upper root collapsed, the addition of the CSF's needed to prevent the variational collapse would represent a redefinition of the valence space. Liu⁶ has found that in some cases the addition of extra orbitals to the valence space in a MCSCF - FOCI calculation can actually yield poorer results and therefore should be avoided.

Our general procedure is to perform a FVMCSCF at several representative points on the surface. The important and marginally important configurations are included in a small MCSCF. Those CSF's with a coefficient smaller than 0.1 at all points are dropped and the final CSF list is chosen. This final list is used in an MCSCF and followed by a CI(SD). If one is only considering the lowest root, repeating the FVCI in terms of NO's can simplify the identification of the important CSF, but for several roots this is not advisable. In BeO, for example, in the NO basis the $1^1\Sigma^+$ state would be described by

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 \quad (1)$$

$$1\sigma^2 2\sigma^2 3\sigma^2 5\sigma^2 1\pi^4 \quad (2)$$

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^2 2\pi^2 \quad (3)$$

but the second and third roots would be nominally described as

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 5\sigma 1\pi^4 \quad (4)$$

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^3 2\pi \quad (5)$$

Starting from (1), (4) and (5) provides a good description of the first and second roots, but starting from (1), (2) and (3) for the first root would necessitate adding other CSF's to describe the second root.

The cases where it is impossible to perform separate optimizations on higher roots fall into two categories: 1) the FVMCSCF calculation collapses and in 2) the limited MCSCF undergoes variational collapse. In the former we do not add any additional configurations. In the case of $\text{CaO } 1\Sigma^+$ states, we overcome this collapse by performing a FVMCSCF (where 8σ , 9σ , 10σ , 3π and 4π are valence orbitals) on the lowest $1\Sigma^+$ state, obtained the natural orbitals, then used these NO's in FVMCSCF for the $2\Sigma^+$ with the 8σ orbital frozen to be the 8σ NO. The important CSF's from both roots included in an MCSCF calculation, and the orbitals optimized for the 1st root. The second root orbitals are then optimized with the 8σ orbital to be the 8σ orbital of the ground state. The second case where the limited MCSCF collapses, arises when the roots are close and the marginal CSF's of the first root are important in preventing root flipping. If the number of CSF's to be added is too large, we freeze an orbital (or orbitals) to be an orbital obtained in limited MCSCF calculation of the ground state. Since we have performed the FVMCSCF calculations we have some measure of the severity of these constraints.

We have noted that if the marginally important CSF's are added to the MCSCF, the energy of the limited MCSCF is within a few milli-hartrees of the FVMCSCF. For MgO the number of CSF's need to approach the FVMCSCF is less than 15 CSF's for all the low lying states. In order to minimize the uncertainty in our calculations we avoid CSF selection whenever possible and if forced to select we keep the cumulative⁷ selection threshold an order of magnitude smaller than the accuracy we seek (1 milli-hartree accuracy). For this reason we choose to include only the important CSF's in the MCSCF - CI. Calculations for MgO using an STO basis set show that this procedure yields Re's and Te's in excellent agreement with experiment.

We should note a few technical aspects of our procedure. The FVMCSCF is made possible by using a second-order MCSCF procedure. Instead of solving the simultaneous equations, we employ a Super-CI technique with a procedure for damping the eigenvector far from convergence. In our implementation a variable number of CI roots can be included in the Hessian. We find that far from con-

vergence including all lower roots improves convergence and only near convergence are all roots coupled in and quadratic convergence observed. The inclusion of all lower CI vectors is an important aspect of the second order MCSCF treatment of excited states. This is to be contrasted to the traditional generalized Brillouin theorem MCSCF where one often needs to shift the diagonal elements of the Super - CI Hamiltonian in order to prevent root flipping. In the case of higher roots of ionic molecules the lower state orbitals or the orbitals of a non-variational SCF do not always provide a good set of starting orbitals. In these situations the use of damping, can be very important. In some cases, the roots flipped as the higher root orbitals were optimized. However, convergence was obtained in these cases by freezing orbitals in the lower root for a few iteration and the eliminating the constraint. In the cases where the apparent variational collapse was a result of a poor choice of starting orbitals, this procedure works well. However one must be careful that this procedure does not lead to a local minima. We should also note that we have found corresponding orbitals very useful in comparing two sets of orbitals. For example, by computing the corresponding orbitals⁸ between the lowest root and a root just as it undergoes variational collapse, it becomes trivial to observe which orbital or orbitals differ in the two states.

The procedure discussed in this paper are based on the assumption that MCSCF calculations containing more than a few hundred CSF's are not routinely possible, however Schaefer¹⁰ has recently reported an MCSCF including more than 10,000 CSF's. Since Schaefer is using a first order method to optimize the orbitals, it is not clear that reasonable convergence will be obtained for a CI(SD) using a general MCSCF reference. Second order MCSCF techniques² have been shown to provide excellent convergence for a general list of CSF's and this method in principle could be used to treat problems including large numbers of CSF's. However, the amount of work needed to construct the Hessian and solve the simultaneous equations could become prohibitively large. If these techniques lead to the ability to routinely perform very large MCSCF calculations, the need to perform a separate CI calculation will be eliminated for most calculations. However, the procedures described will still be useful in determining the list of reference configurations and an initial set of orbitals for the larger MCSCF.

REFERENCES

- ¹ H. F. Schaefer, III, R. H. Klemm, and F. E. Harris, Phys. Rev. **181**, 137(1969).
- ² B. H. Lengsfeld, J. Chem. Phys. in press. While much work has been performed on second order MCSCF theory, this appears to be one of the few completely general second-order MCSCF procedure.
- ³ P. J. Hay and T. H. Dunning, Jr., J. Chem. Phys. **64**, 5077(1976).
- ⁴ K. K. Docken and J. Hinze, J. Chem. Phys. **59**, 6424(1973).

- ⁵A. Banerjee and F. Grein, J. Chem. Phys. 66, 1054(1977).
- ⁶B. Liu Private Communication
- ⁷R. C. Raffanetti, K. Hsu, and I. Shavitt, Theor. Chim. Acta 45, 33(1977).
- ⁸C. W. Bauschlicher, B. H. Lengsfeld, D. M. Silver, D. R. Yarkony, unpublished work.
- ⁹A. T. Amos and G. G. Hall, Proc. Roy. Soc. A263, 483(1961), R. L. Martin and E. R. Davidson, Phys. Rev. A16, 1341(1977).
- ¹⁰B. R. Brooks, W. D. Laidig, P. Saxe, and H. F. Schaefer, J. Chem. Phys. 72 3837(1980).